

A kinetic model for methane oxidation over Pt/Pd/Ce/Al₂O₃ catalysts

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Highlights

- A kinetic model of complete methane oxidation.
- Two modes of inhibition by water.
- A buildup of surface hydroxyls.

1. Introduction

Exhaust aftertreatment of natural gas vehicles has a large focus on reducing emissions of residual methane, one of the greenhouse gases. The technology is based on the catalytic complete oxidation of methane to carbon dioxide and water, which have lower greenhouse potentials comparing to methane. During decades, noble metal-containing catalysts, mainly palladium, are utilized to achieve high methane conversion under operating condition. However, other components of the exhaust, such as water and sulfur dioxide, affect long term activity of the catalysts by poisoning the active sites. Kinetic models provide important information to understand the reaction mechanisms, as well as the models can be used for prediction and optimization of chemical processes. In our work, a well-characterized Pt-Pd-based catalyst was utilized to experimentally investigate the activity and selectivity in methane oxidation varying concentrations of gas phase components: CH₄, NO, CO, O₂ and H₂O. Based on these data, a kinetic model was developed that is capable to simulate features of the transient experiments over time [1].

2. Methods

A sample in a monolith form containing 0.6wt.% Pt, 3.2wt.% Pd and 20wt.% CeO₂ on Al₂O₃ was tested in methane oxidation. The experimental data were utilized in developing a kinetic model using AVL Boost aftertreatment software. One dimension (1D) single channel model was applied and the channel was discretized in the axial direction using 20 grid points with a grid shape factor equal to unity.

3. Results and discussion

The developed kinetic model consists of several reactions, which are shown below with their corresponding rate equations. The first reaction (R1) is a global step for CH₄ oxidation.



It was assumed that adsorbed CH₄ species are rapidly consumed resulting in zero coverage of active sites by methane molecules. It was taken into account that at a large oxygen excess, the rate of methane oxidation is independent of the oxygen concentration. CO₂ is very weakly bound to the precious metal sites and will desorb instantaneously after its formation. Therefore the apparent reaction rate in respect to O₂ and CO₂ is zero order. This resulted in methane reaction rate expression where competitive adsorption of H₂O and NO on active sites are taken into account:

$$r_{\text{R1}} = \frac{k_1 \gamma_{\text{CH}_4} \cdot \theta_{\text{S}^*}}{1 + k_{\text{H}_2\text{O}}^{\text{inhib}} \cdot \gamma_{\text{H}_2\text{O}} + k_{\text{NO}}^{\text{inhib}} \cdot \gamma_{\text{NO}}} \quad (1)$$

The reaction rate is first order with respect to methane concentration, which is consistent with several models in the literature [2-6]. Our experimental results showed that water is significantly decreasing the methane

oxidation, in two modes. Firstly, the activity drops directly when increasing the water concentration, which can be described by the inhibition term in R1. Secondly, there is a slow deactivation of the methane oxidation over time in the presence of water vapor, which could be due to the build-up of hydroxyl species on the active sites. Thus, the experimental data suggest that methane oxidation also depends on active sites S^* ($\theta(S^*) = 1 - \theta(S^*-OH)$) which are affected by slow formation and accumulation of $-OH$ groups according to the reaction (R2).



with a reaction rate given as the following equation (2)

$$r_{R2} = k_2 \cdot \theta_{S^*} \cdot y_{H_2O} \cdot y_{O_2} - k_{-2} \cdot \theta_{S^*-OH} \quad (2)$$

As can be seen in Figure 1, the addition of active sites S^* enables the description of the slow decrease in methane oxidation with time, which is due to the build-up of hydroxyl species on the active sites.

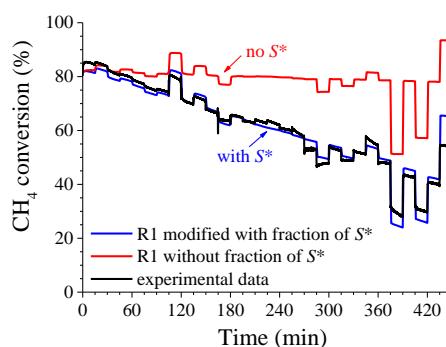


Figure 1. Comparison of the modelling results taking into account active sites S^* (blue curve) and excluding S^* (red curve) from the reaction rate equation (1) of the reaction R1.

4. Conclusions

The developed model provides insights into the inhibition of complete methane oxidation by water over palladium containing catalysts. The first reaction was a global step for CH_4 oxidation, which included inhibition terms for both H_2O and NO . A second reaction was added to the model to account for the formation and decomposition of surface hydroxyls. In the model, the inhibition by water was assigned to the adsorption of H_2O on surface sites resulting in an immediate decrease in CH_4 conversion when increasing the water concentration, as well as to the formation and accumulation of surface hydroxyl groups resulting in a slow activity loss during long term experiments.

References

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Keywords

Oxidation; methane; noble metal, water inhibition.